Electrical Discharge Based Non Catalytic Technique for controlling Total Hydrocarbon Emission in Diesel Exhaust

<u>A. Madhukar¹</u>, B. S. Rajanikanth²

¹ School of Electrical Sciences, Indian Institute of Technology Goa, India, ² Department of Electrical Engineering, Indian Institute of science Bangalore, India

Abstract: The minor pollutants present in diesel exhaust such as hydrocarbons are as toxic and harmful as major pollutants. The control or abatement of theses minor pollutants collectively called as Total Hydrocarbons (THC) in the exhaust is difficult to achieve due to the broad spectrum of the hydrocarbons that encompass groups like alkanes, alkenes, aromatic hydrocarbons, aldehydes, alcohols, ketones etc. As such no single catalyst/adsorbent can address such broad spectrum efficiently. Therefore, any attempt towards controlling these THC is a welcoming step particularly in the real exhaust scenario. In this current work two non-thermal plasma techniques viz., electrical discharge plasma (Direct plasma) and ozone injection (Indirect plasma) were coupled while treating the diesel exhaust for possible mitigation of total hydrocarbons (THC). The work is intended to provide a cleaning system which is non-catalytic, non-adsorbent and non-thermal plasma based one leading to less utilization of electrical energy and long lasting.

Keywords: Non Thermal Plasma, Ozone injection, Diesel exhaust, Cascaded Plasma, Total hydrocarbons,

1.Introduction

Hydrocarbon (HC) emissions are composed of unburned fuels as a result of insufficient temperature which occurs near the cylinder wall. Hydrocarbons consist of hundreds of species, such as alkanes, alkenes, aldehydes and aromatics. In Diesel engines, the fuel type, engine adjustment, and design, all affect the content of hydrocarbons. They constitute about 50% of total HC emission into the atmosphere. The majority of the harmful effects of hydrocarbon pollution are not due to the hydrocarbon themselves, but the products of photochemical reactions in which they are involved such as ozone and smog. Many HCs can cause serious health problems damaging the nervous, reproductive, liver and kidney systems. Some HCs are recognized as potential human carcinogens. Slightly high dose of exposure to many of the HCs leads to wheezing, chest pain, inflammation and ulceration of the mouth and stomach.

The application of non-thermal plasma (NTP) or electrical discharge plasma for gaseous pollutant treatment is still in its initial stages for the past two decades and very little work has been reported in the abatement of THC by NTP in any exhaust source. The exhaust gas when it gets exposed to the electrical discharge plasma there will be production of several charged species including energetic electrons, excited species, ions, metastable and radicals. It is these radicals that are mainly responsible for carrying out necessary chemical reactions such as ionization, reduction, recombination, decomposition etc. upon reacting with gaseous pollutants. It is now well understood that in the case of plasma treatment of NOx present in diesel exhaust it is the oxidizing reactions which are prevalent converting NO to NO₂[1-6]. The same oxidizing reactions may or may not happen with THC when exhaust is exposed to plasma. One can expect formation of CO₂, H₂O or oxidized gaseous components which are non-hazardous in nature.

In this work exhaust from diesel engine was exposed to high energetic electrons or highly oxidizing agents such as ozone. The exhaust was at laboratory temperature (room temperature) and the flow was a controlled one. The study is aimed at reducing the total hydrocarbons present in the exhaust or at least convert them to non-hazardous ones without resorting to additional treatments such as adsorption/catalysis. In other words, the engine exhaust was treated either with direct electrical discharge plasma or with ozone injection or with a combination of aforementioned two types of plasmas.

It was observed that by cascading discharge plasma with ozone the THC reduction/conversion was enhanced when compared to that with individual plasma/ozone treatment. Such a combination of plasma/ozone treatment for THC reduction is rather a new approach in the NTP fraternity. Further, for the first time an attempt has been made in this work (to the extent possible) to provide the possible pathways for THC reduction/conversion. In addition to THC there is also a possibility of reduction of other organic gases such as aldehydes, ketones etc., though, not quantized in the present work.

2. Experimental Setup

The Studies were carried out in controlled laboratory conditions by utilizing electrical discharge based non thermal plasma and ozone injection setup. The current aim is to understand the possible reaction pathways of THC reduction under Plasma exposure. The solid particulate matters were filtered out to facilitate the THC reduction/conversion study. A 5 kVA petro diesel generator was used at no load condition as source of THC followed by a filtering unit of 5 micron size. The exhaust flow was regulated at 8 lpm to the treatment zone. For direct plasma studies 50kV high voltage power frequency AC source source was used, for indirect plasma studies the ozone was produced using a dry air cylinder utilizing a 25 kV repetitive pulse source. The dielectric barrier discharge (DBD) reactor were used for both direct and indirect plasma. The DBD reactor consist of a concentric metallic discharge electrode inside a 28 cm long quartz glass tube. The Discharge were happening in the 2 mm volume inside the DBD reactor. In case of indirect plasma a separate mixing chamber was installed were ozone was reactive with the exhaust. In this work two aaproaches has been adopted for complete treatment of exhaust as shown in Fig 1. For measuring the applied voltage a voltage divider (2000:1, 50kVp-p, Ep-50K, PEEC, Japan) which was connected to the digital storage oscilloscope (DL 1540, 200 MS/s, Yokogawa, Japan) was facilitated. The generated ozone was measured by ozone analyzer (AES-LC 3000 Aurozone, India) and the exhaust gas components i.e. total hydrocarbon was measured by flame ionization detector (FID) based THC analyzer (Mexa 1170HFID, Horiba Ltd., Japan).



Fig 1. Outline of Experimental setup used for Cascaded plasma

3. Results and Discussion

In any experimental work of current nature, it is very essential to understand nature of the chemical reactions that would have been triggered by the formation of radicals or reactive molecules upon application of direct/indirect electrical discharges. Owing to the presence of several hydrocarbons and due to the formation of several chemically active species in plasma, it will not be an easy task to attribute a specific reaction for the reduction/conversion of THC when the exhaust gets exposed to plasma or ozone injection. At this juncture it is worth mentioning that the plasma-based THC reduction studies in diesel exhaust has not been reported much and further, there is scant information about the reaction routes leading to THC reduction. Through this paper attempt has been made to summarize all possible reaction pathways based on the knowledge of synthetic HC decomposition under the influence of plasma species and utilize these pathways to substantiate the findings of the current research. In current work diesel exhaust was exposed to plasma produced radicals in direct plasma chamber and highly reactive O₃/ H₂O₂ in mixing chamber in case of indirect plasma. The reaction pathways can be summerized as below [7]:

Group-A: Formation of O, OH, HO₂ radicals & O₃/H₂O₂ molecules under direct and indirect plasma

$O_2 + e$	\rightarrow	$O + O^+ + 2e$	(1)
$H_2O + e$	\rightarrow	$OH + H^+ + 2e$	(2)
$O + H_2O \rightarrow$	2OH		(3)
$O_3 + H$	\rightarrow	$O + HO_2$	(4)
$O_2 + O$	\rightarrow	O ₃	(5)
$O + O_3$	\rightarrow	2O ₃	(6)
$H_2O + O_3$	\rightarrow	$O_2 + H_2O_2$	(7)

Group-B: Direct plasma (O radicals)

$Alkanes$ $CH_4 + O$ $CH_3 + O \rightarrow$ $CH_3O + O$ CH_3+O $HCHO +O$	$ \begin{array}{c} \rightarrow \\ CH_{3}O \\ \rightarrow \\ \rightarrow \\ \rightarrow \end{array} $	CH ₃ +OH HCHO + OH HCHO +H HCO* +OH	(8) (9) (10) (11) (12)
$C_{4}H_{10} + O$ $C_{4}H_{9} + O$ $CH_{3}CHO + O$ $CH_{3}CO + O$	$ \begin{array}{c} \rightarrow \\ \rightarrow \\ \rightarrow \\ \rightarrow \end{array} $	C4H9 +OH CH3CHO + C2H5 CH3CO +OH CHCHO +OH	 (13) (14) (15) (16)
$Alkenes$ $C_{2}H_{4} + O$ $C_{2}H_{3} + O$ $C_{2}H_{3} + O$	\rightarrow \rightarrow \rightarrow	$\begin{array}{l} C_2H_3+OH\\ C_2H_2+OH\\ CH_3+CO \end{array}$	(17) (18) (19)
$\begin{array}{l} C_{3}H_{6}+O\\ C_{3}H_{6}+O\\ C_{3}H_{6}+O\\ C_{3}H_{6}+O\\ C_{3}H_{6}+O\\ C_{3}H_{6}+O\end{array}$	$ \begin{array}{c} \rightarrow \\ \rightarrow \\ \rightarrow \\ \rightarrow \\ \rightarrow \\ \rightarrow \end{array} $	$C_{3}H_{5} + OH$ $C_{2}H_{5} + HCO$ $CH_{3} + CH_{2}CHO$ $CH_{3} + H + CHCHO$ $C_{3}H_{6}O$	(20) (21) (22) (23) (24)
$Alkynes C_2H_2 + O C_2H_2 + O$	\rightarrow \rightarrow	$\begin{array}{c} CH_2+CO\\ CCHO+H \end{array}$	(25) (26)
Aromatic Hydroc, $C_{6}H_{6} + O$ $C_{6}H_{5} CH_{3} + O$ $C_{6}H_{4} (CH_{3})_{2} + 2C$	$\begin{array}{c} \text{arbons} (M) \\ \rightarrow \\ \rightarrow \\) \rightarrow \end{array}$	fono) $C_6H_5 + OH$ $C_6H_5CH_2O + H$ $C_6H_4 (CH_2O)_2 + 2H$	(27) (28) (29)
Aldehydes $CH_3CHO + O$ HCHO + O $CH_3CO + O$ $CH_3O + O$ Crown C: Dira	\rightarrow \rightarrow \rightarrow \rightarrow	CH ₃ CO +OH HCO* +H CH ₃ O +CO HCHO + OH	(30) (31) (32) (33)
Alkanes C ₂ H ₆ + OH	→	C ₂ H ₅ +H ₂ O	(34)
Alkenes C2H4 + OH CH3 + OH HCHO + OH	$ \begin{array}{c} \rightarrow \\ \rightarrow \\ \rightarrow \end{array} $	CH ₃ + HCHO HCHO + H ₂ O HCO* +H ₂ O	(35) (36) (37)
$C_{3}H_{6} + OH$ $CH_{3}CHO + OH$ $CH_{3}CHO + OH$ $CH_{3}CO + OH$	$ \begin{array}{c} \rightarrow \\ \rightarrow \\ \rightarrow \\ \rightarrow \\ \rightarrow \end{array} $	$CH_3 + CH_3CHO$ $CH_3 + CO + H_2O$ $CH_3CO + H_2O$ CH_3COOH	(38) (39) (40) (41)

 $CH_2CO + H_2O$

 $CH_3OH + HCHO$

(42)

(43)

 $CH_3CO + OH$

 $CH_2CO + OH$

\rightarrow	$C_2H_5 + HCHO$	(44)
\rightarrow	$HCO* + H_2O$	(45)
\rightarrow	$HCOOH^{**} + H$	(46)
\rightarrow	$C_{3}H_{6}OH + M$	(47)
	$\begin{array}{c} \rightarrow \\ \rightarrow \\ \rightarrow \\ \rightarrow \end{array}$	$\begin{array}{ll} \rightarrow & C_2H_5 + HCHO \\ \rightarrow & HCO^* + H_2O \\ \rightarrow & HCOOH^{**} + H \\ \rightarrow & C_3H_6OH + M \end{array}$

Aromatic Hydrocc	irbons	(Mono/Polycyclic)	
PAH + OH	\rightarrow	PAH-OH	(48)
PAH + OH + O2	\rightarrow	Oxidized PAH	(49)
MAH + OH	\rightarrow	COx	(50)

Group-D: Direct plasma (HO₂ radicals)

$C_2H_4 + HO_2$	\rightarrow	$C_2H_4O + OH$	(51)	
$C_3H_6 + HO_2$	\rightarrow	$C_3H_6O + OH$	(52)	
$C_3H_6 + HO_2$	\rightarrow	$C_2H_5 + H_2O_2$	(53)	

Group-E: Indirect plasma (O₃)

$C_4H_8 + O_3$	\rightarrow	$C_3H_6O + HCHO$	(54)
$C_4H_8 + O_3$	\rightarrow	CH ₃ CHO + CH ₃ HCOO	(55)
$C_4H_8+O_3\\$	\rightarrow	2CH ₃ CHO	(56)
$C_2H_4 + O_3$	\rightarrow	2HCHO + O	(57)
$C_2H_4 + O_3$	\rightarrow	HCHO + HCOOH**	(58)
$HCOOH + CH_4$	\rightarrow	$CH_{3}OH + HCHO$	(59)
HCHO + O	\rightarrow	HCO* +OH	(60)
$C_{6}H_{6} + 3O_{3}$	\rightarrow	$3(CHO-CHO) + 3H_2O_2$	(61)
$C_6H_5CH_3 + O_3$	\rightarrow	C ₆ H ₅ CHO ₂ + H ₂ O	(62)

Group-F: Direct & Indirect plasma (H₂O₂ *applicable to raw exhaust*)

$HCHO + H_2O_2$	\rightarrow	$HCOOH^{**} + H_2O$	(63)
$C_4H_8 + H_2O_2$	\rightarrow	$C_4H_7OH + H_2O$	(64)
$C_6H_6 + H_2O_2$	\rightarrow	C ₆ H ₅ OH	(65)

Group-G: Reduction of Total organic gases (aldehydes, carboxylic acid, aromatic HC, alkynes)

HCO* + O	\rightarrow	CO + OH	(66)
HCO* + O	\rightarrow	$CO_2 + H$	(67)
HCO* + OH	\rightarrow	$H_2O + CO$	(68)
$HCO* + HO_2$	\rightarrow	$OH + H + CO_2$	(69)
HCOOH** + OH -	\rightarrow	$H_2O + CO_2 + H$	(70)
HCOOH**	\rightarrow	$H_2O + CO$	(71)
$C_6H_6 + OH$	\rightarrow	$CO_2 + CO + H_2O$	(72)

The study was carried out on a reduced exhaust flow rate of 8 lpm at room temperature with solid particulate filtered. The exhaust was treated in the raw conditions without filtering out the moisture to reap the benefits of the effect of hydroxyl/hydroperoxyl radicals on HC conversion. Further, the filtration of solid soot particulate was necessary as the study was aimed at understanding the role of gaseous and charged plasma species/oxidizing agents on the HC reduction/conversion/oxidation. Flame ionization detector (FID) was used for the HC analysis and the reduction/removal of HCs was discussed keeping in mind the limitations of the FID measurement with respect to alcohol/aldehyde/ketone/oxidized-HCs formation. After studying the THC variations with individual treatments of direct plasma and ozone injection, attempt was also made cascading the two treatments and studying its combined effect on THC reduction/variation. Such a cascaded arrangement has yielded successful DeNOx results [8] and hence, being tested for reduction/conversion of THC.

Fig 2 & 3 shows the effect of cascading direct and indirect plasma by varying specific energy (Fig 2) and ozone concentration (Fig 3) In this cascade treatment the THC reduction/conversion efficiency reached a maximum of about 95~96% for specific energy of about 70 J/L and at an ozone concentration of about 1656 ppm. Higher ozone concentrations have vielded better THC reduction/conversion efficiency for a given specific energy as shown in Fig. 2. The increased THC conversion in cascade arrangement can be attributed for two reasons: one is that the butene in the exhaust while passing through the plasma shower goes unabated (not reacting) in presence of plasma-radicals. However, when it gets exposed to ozone in mixing chamber it may get converted to oxidized HCs. Secondly, the ethylene in the exhaust has higher probability of getting converted to aldehyde/carboxylic acid/alcoholic groups (reactions 57-60) when compared to that with O radical (reaction 17). Similarly, the benzene present in the exhaust may have higher probability of forming glyoxal (aldehyde variant) upon reacting with ozone (reaction 61) when compared to forming phenyl with O radical (reaction 27). Apart from increased THC conversion there is also a possibility of THC reduction in the plasma and ozone injection chambers owing to the reduction of aldehydes/carboxylic acid species to H₂O/CO/CO₂ (reaction 66-72).

Fig 4 & 5 present the results of THC treatment of diesel exhaust in the cascade arrangement when the order of treatment was reversed i.e. exhaust was first allowed to get mixed with ozone followed by exposure to plasma-radicals.

The overall THC conversion/reduction was about 83%, more or less similar to the previous arrangement (i.e. Direct plasma + O3 injection) amd hence above reaction pathways as discussed above are valid in both the cases. Fig. 2-5 infer that the order of direct/indirect plasma connection do not matter for THC treatment

As mentioned before caution should be exercised in the interpretation of FID analyzer's readings as oxidized $HCs/CO/CO_2$ are all treated alike in the FID. The ambiguity surrounding the measurement of THC, i.e. whether THC has been reduced or converted, can be eliminated by additionally measuring the oxidized HCs using a gas chromatograph-based analyzer which will be part of authors' future study. The combined reduction of NOX and THC may require additional treatment utilizing adsorbents/catalyst can be authors another future study.



Fig 2. Variation of THC in cascaded direct plasma + Ozone injection treatment: Effect of ozone injection



Fig 3. Variation of THC in cascaded direct plasma + Ozone injection treatment: *Effect of applied plasma energy*



Fig. 4 Variation of THC in cascaded Ozone injection + direct plasma treatment: Effect of ozone injection



Fig 5. Variation of THC in cascaded Ozone injection + direct plasma treatment: Effect of applied plasma energy

4. Conclusion

In current work the cascaded effect of direct and indirect plasma was studied for THC reduction of diesel engine exhaust at laboratory conditions. The following findings can be itemized:

- In principle, a non-catalytic/non-adsorbent based THC reduction/conversion may be possible by utilizing electrical discharge plasma as evident from laboratory study.
- Possible reaction pathways have been identified to address THC reduction/conversion in diesel exhaust when exposed to discharge plasma/ozone injection.
- Cascaded plasma + ozone injection offers a novel way in controlling THC emission to the tune of 83-96% in controlled exhaust flow conditions.

5. References

[1] P.Talebizadeh, M.Babaie et al. The role of non-thermal plasma technique in NO*x* treatment: A review. Renewable and sustainable energy review, 40 (2014)

[2] J.O. Chae, Non-thermal plasma for diesel exhaust treatment, Journal of electrostatics,57 (2003)

[3] Apeksha Madhukar, Pragati K.M., Janardhana M, B.S.Rajnaikanth, Agricultural rice husk waste for cleaning diesel exhaust pre-treated by non-thermal direct/indirect plasma, International symposium on non-thermal plasma, July 1-5.(2018)

[4] Apeksha Madhukar, B.S. Rajanikanth Plasma/adsorbent system for NOx treatment in diesel exhaust: a case study on solid industrial wastes. International journal of environmental science and technology (2018)

[5] Anusuya B, Rajanikanth B.S., Estimation of power input to complex dielectric barrier discharge reactor geometries used in NOx cleaning. IEEE Trans. Dielectric and Electrical Insulation, 22 (2015)

[6] Muhammad F.M, Xindi F., Yanjun L., Yawar A., Hongtao W., Wenjing L. Volatile organic compounds (VOCs) removal in non-thermal plasma double dielectric barrier discharge reactor. Journal of Hazardous Materail, 347 (2018)

[7] Apeksha M, Rajanikanth B.S., Cascaded Plasma- ozone injection system: A novel approach for controlling THC emission in diesel exhaust, 39(2019)

[8] Apeksha M, Rajanikanth B.S. (2018) Augmenting NOx reduction in diesel exhaust by combined plasma/ozone injection technique: A laboratory investigation, IET Trans. High Voltage,3 (2018)